Exergy Analysis Of A System Using A Chemical Heat Pump To Link A Supercritical Water-cooled Nuclear Reactor And A Thermochemical Water Splitting Cycle

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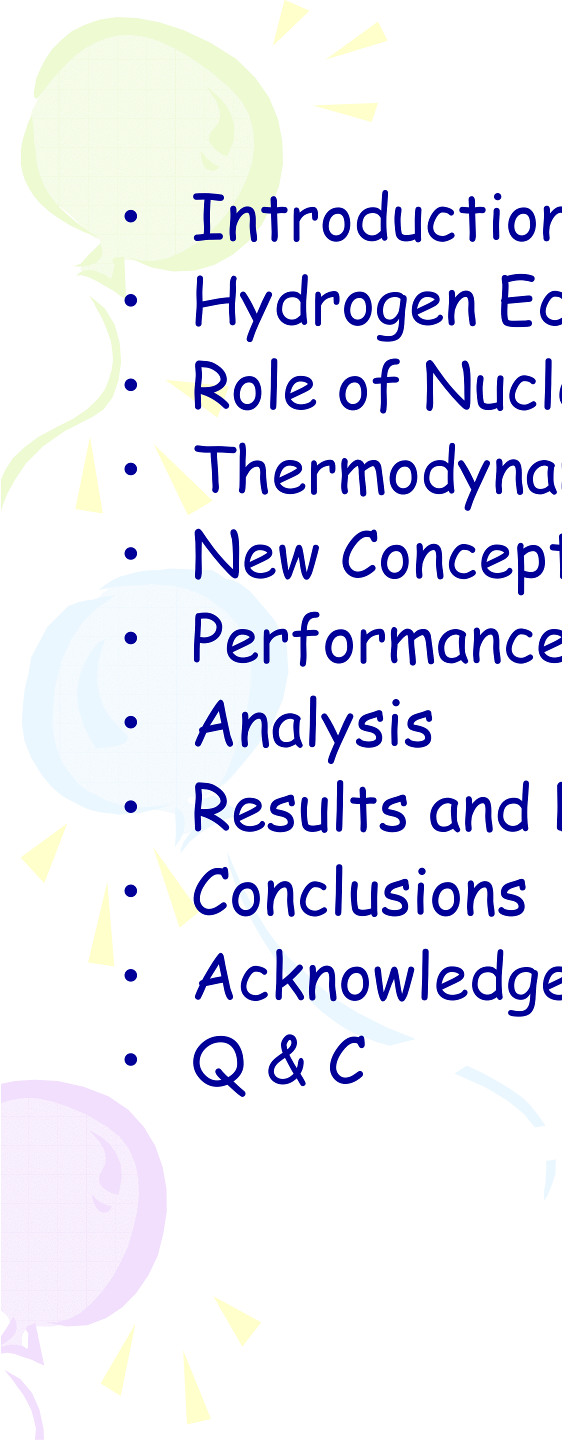
OUTLINE



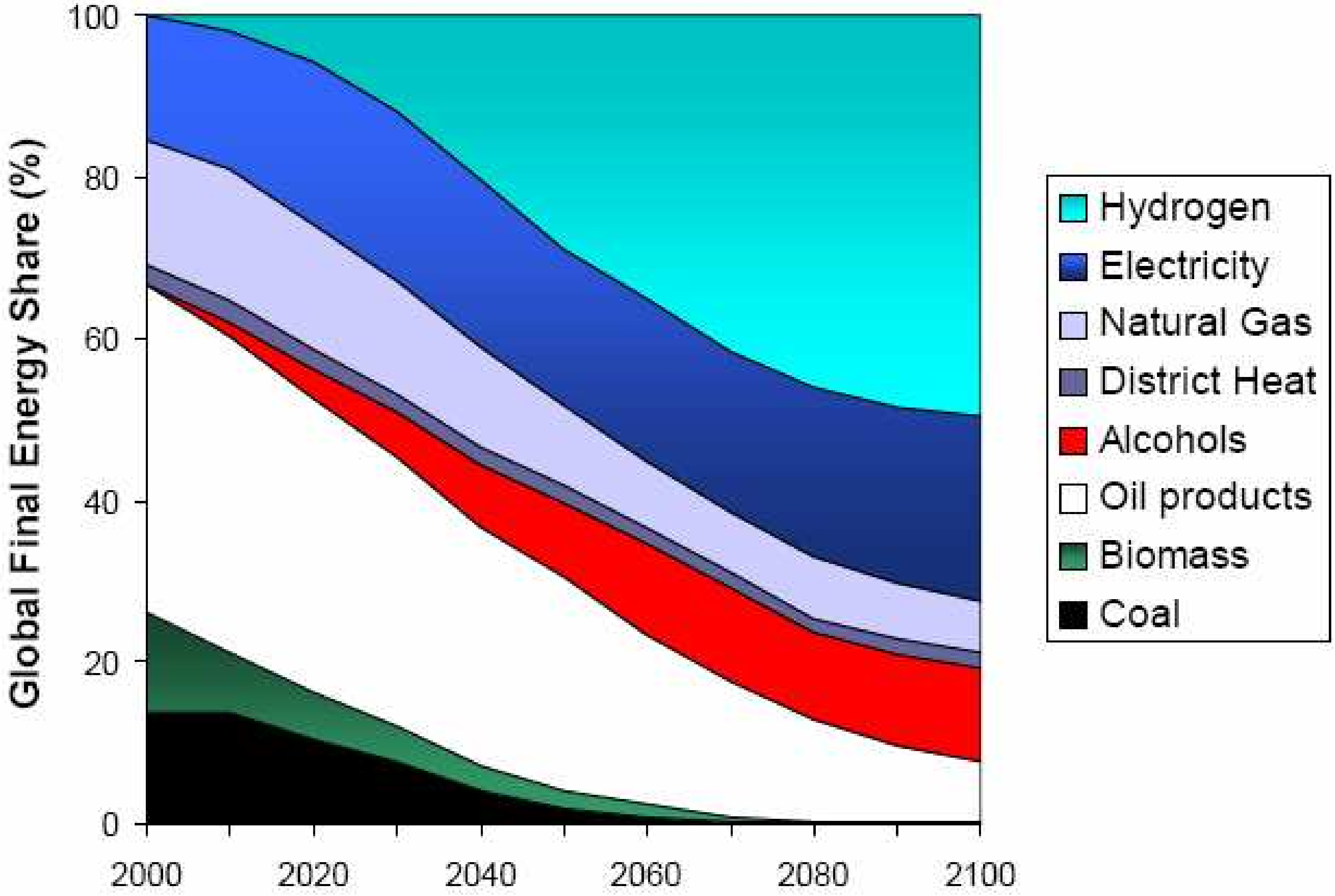
- Introduction
- Hydrogen Economy
- Role of Nuclear Energy
- Thermodynamic Aspects
- New Concept
- Performance Investigation
- Analysis
- Results and Discussion
- Conclusions
- Acknowledgement
- Q & C

Some Significant H_2 Projects in Canada

- Hydrogen highway
- Hydrogen corridor
- Hydrogen village
- Hydrogen airport
- Hydrogen island
- Nuclear hydrogen at UOIT
- etc.

☛ Why such projects?

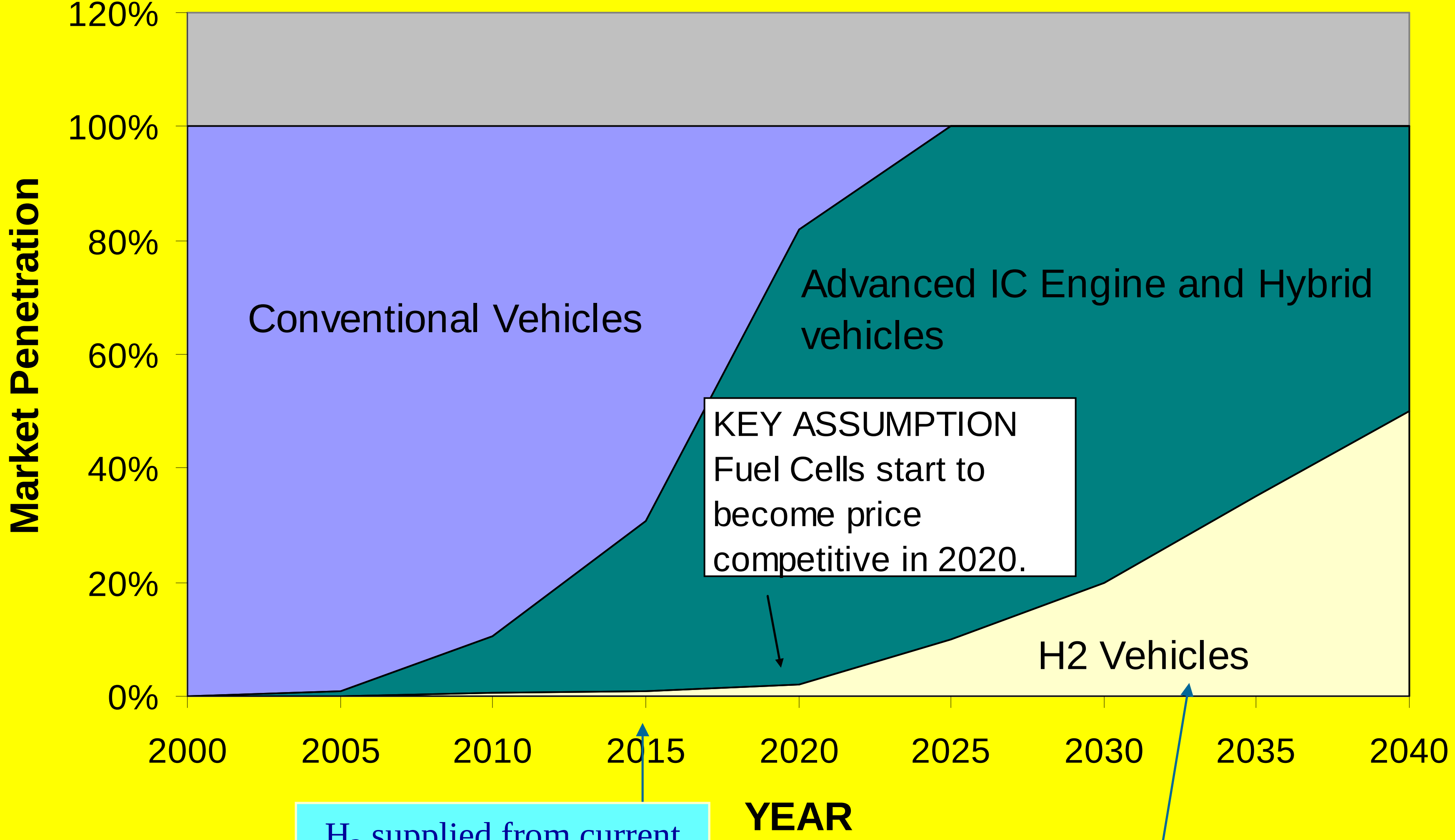
- There are ~17 million light-duty cars and trucks on Canada's roads today, which create about 12% of the country's greenhouse gas emissions (Environmental Defence Canada, 2006).
- In 2000, 5,000 people in Canada died prematurely because of air pollution (Environmental Defence Canada, 2006).



Evolution of global market shares of different final-energy carriers for the period 1990-2100 based on the scenario by Barreto et al. [5]. The alcohols category includes methanol and ethanol.

Scenario One - Evolution of Transportation

Source: Ricardo (2004).

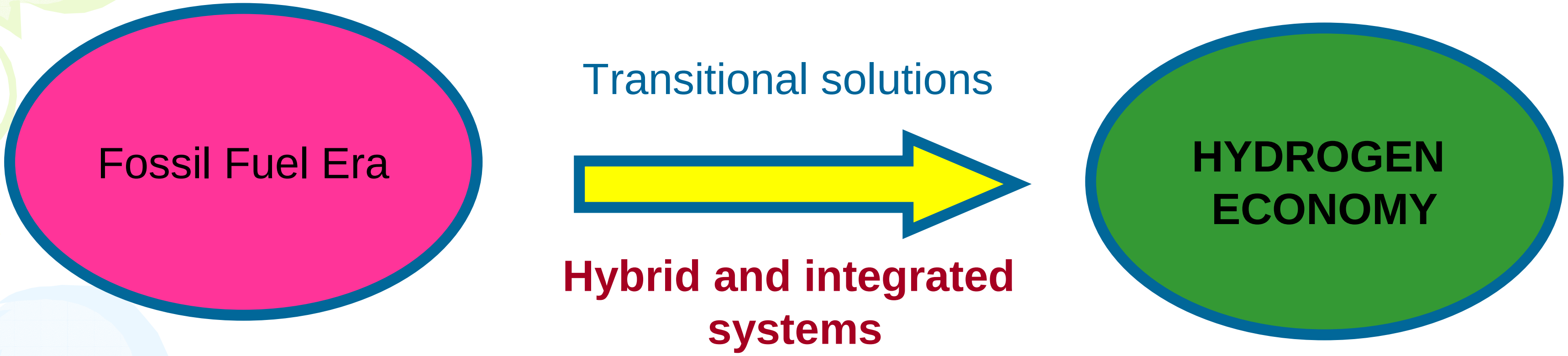


KEY ASSUMPTION
Fuel Cells start to become price competitive in 2020.

H_2 supplied from current sources.and new units, possibly electrolysis

Growing H_2 infrastructure driven by public demand

TRANSITIONAL SOLUTIONS



Fossil Fuel Era

Transitional solutions

Hybrid and integrated systems

HYDROGEN ECONOMY

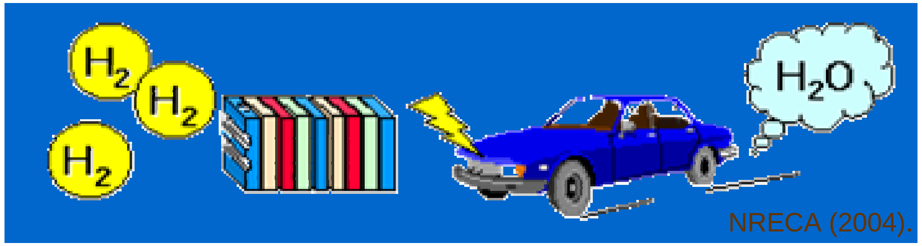
Key items:

- Policies
- Models
- Performance tools
- Technologies
- Infrastructure
- Commercialization
- etc.

Key players:

??????????

Hydrogen + Fuel Cells = Electricity



NRECA (2004).

Transportation =

Higher Fuel Efficiency

+ Zero Pollution

CANDU Technology
Evolutionary Development for 60 Years

1940's – Heavy Water Moderated Research Reactors (Gen-0)
1950's – CANDU Prototype (Gen-I)
1960's – Large CANDU Commercial Plants (Gen-I+)
1970's – Multi-Unit CANDU Plants (Gen-II)
1980's – CANDU-6 (Gen-II+)
1990's – CANDU-9 (Gen-III)
2000's – ACR (Gen-III+)
2010's – SCWR (Gen-IV)

Evolutionary product innovation strategy Suppiah (2006).

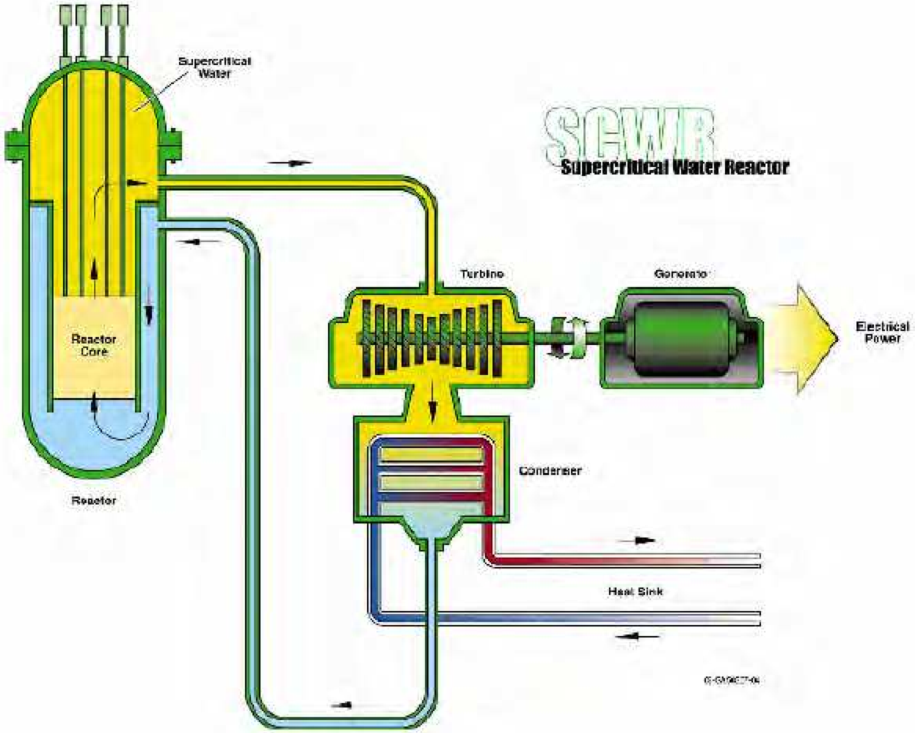
GenIV Reactor Systems

- Gas-Cooled Fast Reactor (GFR)
- Lead-Cooled Fast Reactor (LFR)
- Molten Salt Reactor (MSR)
- Sodium-Cooled Fast Reactor (SFR)
- Supercritical-Water-cooled Reactor (SCWR)
- Very-High-Temperature Reactor (VHTR)

→ Canada's primary interest: SCWR

Key Advantages

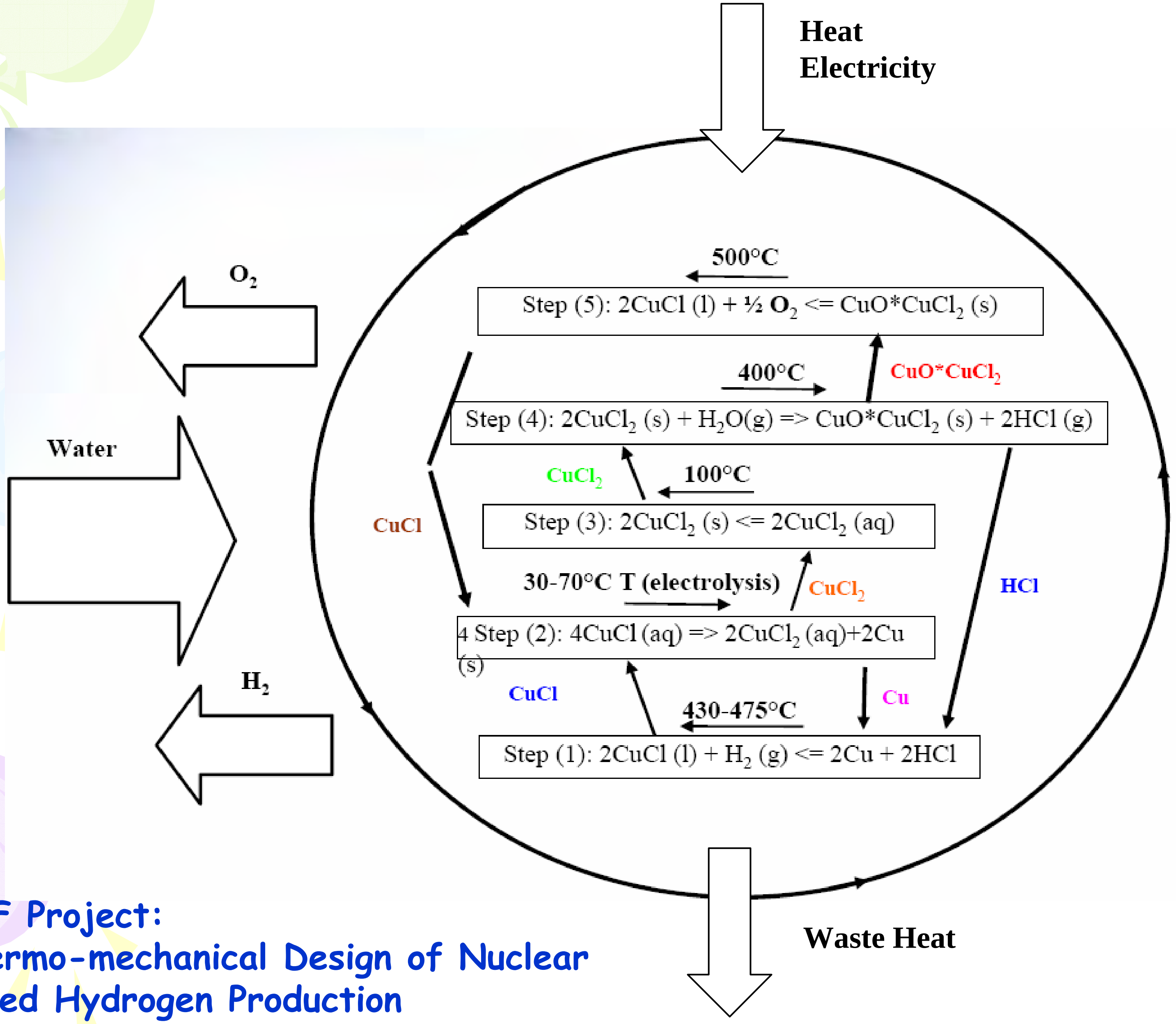
- Major economic advantage
- High level of safety
- Flexible fuel cycle system(s)
- Direct and Indirect Production of H_2
- Direct SCW cycle (no steam generators)
- Higher efficiency (>44%)
- Turbine technology available
- Operating conditions:
  - Pressure: ~25 MPa.
  - Outlet Temperature: 500°C-650°C



Suppiah (2006).

→ Prime goal: To play a key role in hydrogen economy

Cu-Cl Cycle for H_2 Production



Step (5): $2CuCl\,(l) + \frac{1}{2}\,O_2 \Leftarrow CuO{*}CuCl_2\,(s)$

Step (4): $2CuCl_2\,(s) + H_2O(g) \Rightarrow CuO{*}CuCl_2\,(s) + 2HCl\,(g)$

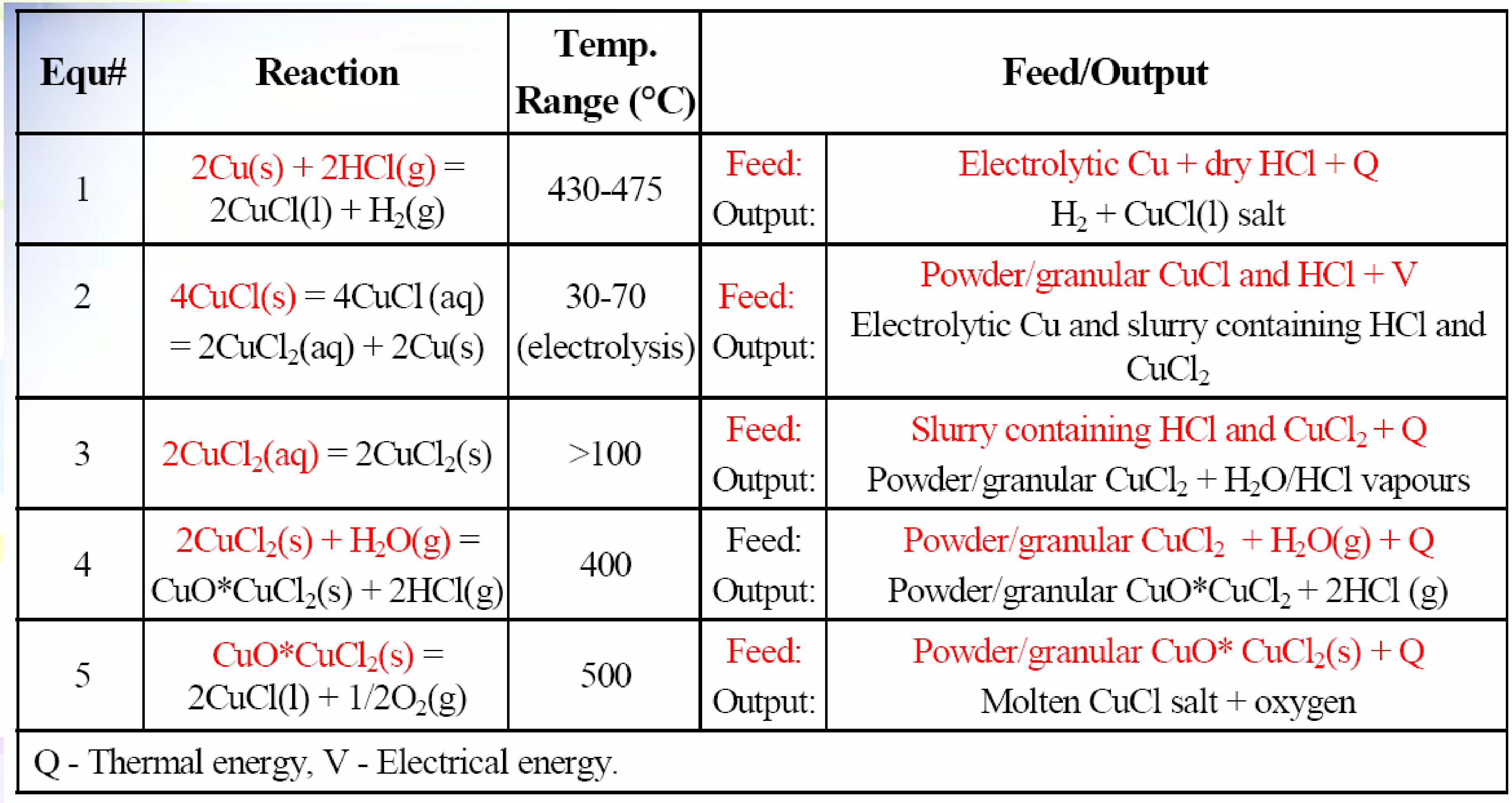
Step (3): $2CuCl_2\,(s) \Leftarrow 2CuCl_2\,(aq)$

4 Step (2): $4CuCl\,(aq) \Rightarrow 2CuCl_2\,(aq) + 2Cu\,(s)$

Step (1): $2CuCl\,(l) + H_2\,(g) \Leftarrow 2Cu + 2HCl$

ORF Project:
Thermo-mechanical Design of Nuclear Based Hydrogen Production

Thermochemical Reactions in the Cu-Cl Cycle



Equ#	Reaction	Temp. Range (°C)	Feed/Output	
1	$2Cu(s) + 2HCl(g) = 2CuCl(l) + H_2(g)$	430-475	Feed: Output:	Electrolytic Cu + dry HCl + Q H_2 + CuCl(l) salt
2	$4CuCl(s) = 4CuCl(aq) = 2CuCl_2(aq) + 2Cu(s)$	30-70 (electrolysis)	Feed: Output:	Powder/granular CuCl and HCl + V Electrolytic Cu and slurry containing HCl and $CuCl_2$
3	$2CuCl_2(aq) = 2CuCl_2(s)$	>100	Feed: Output:	Slurry containing HCl and $CuCl_2$ + Q Powder/granular $CuCl_2$ + H_2O/HCl vapours
4	$2CuCl_2(s) + H_2O(g) = CuO{*}CuCl_2(s) + 2HCl(g)$	400	Feed: Output:	Powder/granular $CuCl_2$ + $H_2O(g)$ + Q Powder/granular $CuO{*}CuCl_2$ + 2HCl (g)
5	$CuO{*}CuCl_2(s) = 2CuCl(l) + 1/2O_2(g)$	500	Feed: Output:	Powder/granular CuO* $CuCl_2(s)$ + Q Molten CuCl salt + oxygen

Q - Thermal energy, V - Electrical energy.

Key Advantages of Cu-Cl Cycle

- High efficiency (from Scoping Flowsheet Methodology) - 41%
- Electrical energy - 39% of total energy consumption
- Low temperature requirement for heat source <530°C
- Temperature requirement for heat source met by currently existing power plant technology (e.g. thermal stations using supercritical water cycles)
- Potentially suitable to couple with AECL's SCWR reactor
- Materials-of-construction and corrosion issues more tractable at 530°C than at higher temperatures required by other cycles
- Inexpensive raw materials as recycle agents (for example, compared to iodine for S-I cycles)
- No requirement for catalyst in thermal reactions
- No significant side reactions (?)
- Complete conversions to desired products in thermal reactions (?)

Suppiah (2006).

PRESCRIPTION

- More efficient and effective energy systems and applications
- More environmentally benign energy systems and applications
- More cost effective energy systems and applications
- Better energy and exergy security measures

as well as

- Right energy and exergy strategies and policies

☛ More sustainable FUTURE………

ENERGY → EXERGY

- Energy is EVERYTHING!
- Efficient Energy Use
- Exergy

THERMODYNAMIC ASPECTS

- **The First Law of Thermodynamics-The law of conservation of energy ➔ ENERGY**
  - is about how energy is never made or lost (it just changes forms).
  - is phrased as "*You can't get something for nothing*".

- **The Second Law of Thermodynamics ➔ EXERGY**
  - refers to the inefficiencies and impossibility to have ideal efficiency in all energy processes, due to irreversibilities.
  - is the linkage between entropy and usefulness of energy.
    - ***Entropy is the degree of disorder.***
  - is phrased as "*You can't even get all you pay for*".

ENERGY

- is dependent on the parameters of matter or energy flow only, and independent of the environment parameters.
- is guided by the first law for all processes.
- is a measure of quantity.

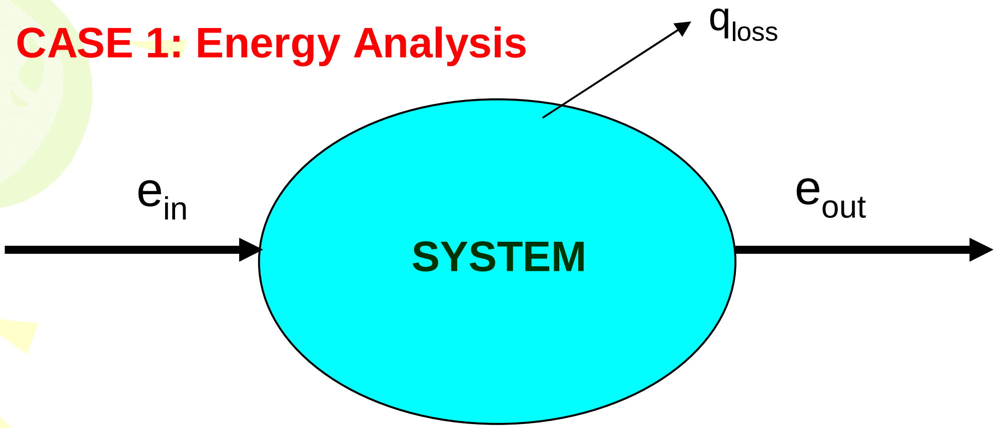
EXERGY

- is dependent both on the parameters of matter or energy flow and on the environment parameters.
- is guided by the second law for all irreversible processes.
- is a measure of quantity and quality.

WHY EXERGY?

- An effective method using the conservation of mass and conservation of energy principles together with the second law for the design and analysis of energy systems.
- A way to study how we can make systems and processes more efficient.
- An efficient technique revealing whether or not and by how much it is possible to design more efficient energy systems by reducing the inefficiencies.
- A suitable technique for furthering the goal of more efficient energy-resource use.
- A key tool for determining the locations, types, and true magnitudes of wastes and losses.
- A measure of usefulness, quality or potential of a stream to cause change.
- A tool for sustainable development.

CASE 1: Energy Analysis

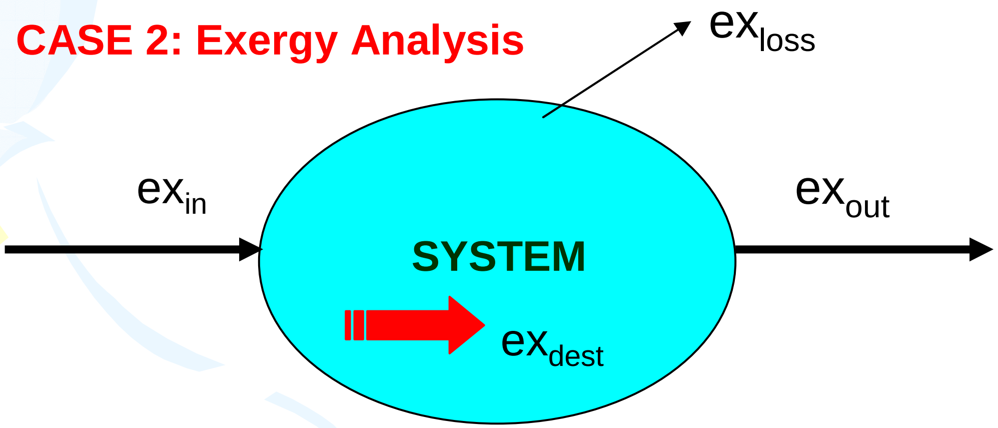


$\eta = e_{out} / e_{in}$

Energy balance: $e_{in} = e_{out} + q_{loss} \rightarrow e_{out} = e_{in} - q_{loss}$

……

CASE 2: Exergy Analysis

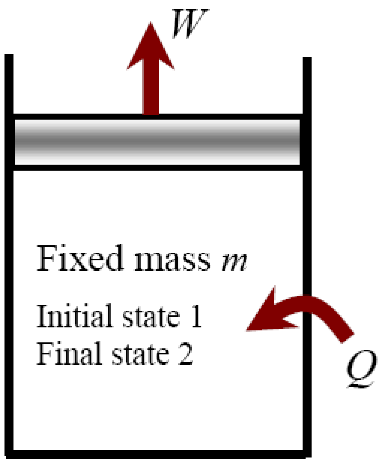


$\psi = ex_{out} / ex_{in}$

Exergy balance: $ex_{in} = ex_{out} + ex_{loss} + ex_{dest} \rightarrow ex_{out} = ex_{in} - ex_{loss} - ex_{dest}$

The result: $ex_{out} < e_{out}$

Balance equations for (a) closed and (b) open systems



Closed system (fixed mass)

Mass balance:

$$m_1 = m_2 = \text{constant}$$

Energy balance:

$$Q = m(u_2 - u_1) + W$$

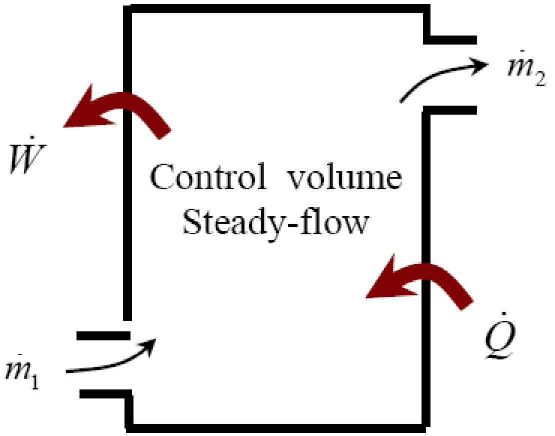
Entropy balance:

$$\frac{Q}{T_s} + S_{\text{gen}} = m(s_2 - s_1)$$

Exergy balance:

$$\left(1 - \frac{T_0}{T_s}\right)Q - [W - P_0(V_2 - V_1)] - Ex_{\text{destroyed}} = Ex_2 - Ex_1$$

(a)



Open system (steady-flow process)

Mass balance:

$$\dot{m}_1 = \dot{m}_2$$

Energy balance:

$$\dot{m}_1 h_1 + \dot{Q} = \dot{m}_2 h_2 + \dot{W}$$

Entropy balance:

$$\frac{\dot{Q}}{T_s} + \dot{m}_1 s_1 + \dot{S}_{\text{gen}} = \dot{m}_2 s_2$$

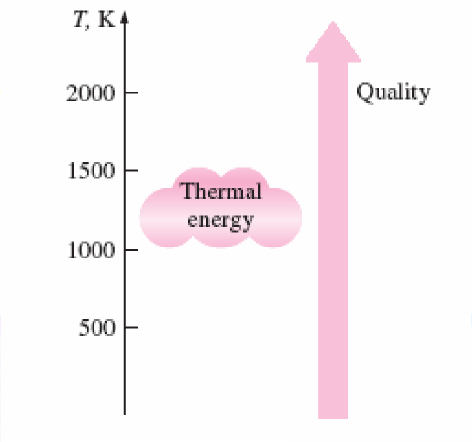
Exergy balance:

$$\left(1 - \frac{T_0}{T_s}\right)\dot{Q} + \dot{m}_1\psi_1 = \dot{m}\psi_2 + \dot{W} + \dot{E}x_{\text{destroyed}}$$

(b)

Energy and exergy efficiencies for some typical energy uses.

Utilization	*Energy Efficiency*	*Exergy Efficiency*
Electricity generation or traction (large scale)	0.90-0.95	0.30
Industrial steam production	0.85	0.25
Fluidized bed electricity generation	0.40-0.45	0.40-0.45
Transportation (diesel powered)	0.40	0.10
Transportation (gasoline powered)	0.25	0.10
Space heating or cooling	0.50-0.80	0.05
Domestic water heating	0.50-0.70	0.05
Incandescent lightbulb	0.05	0.05



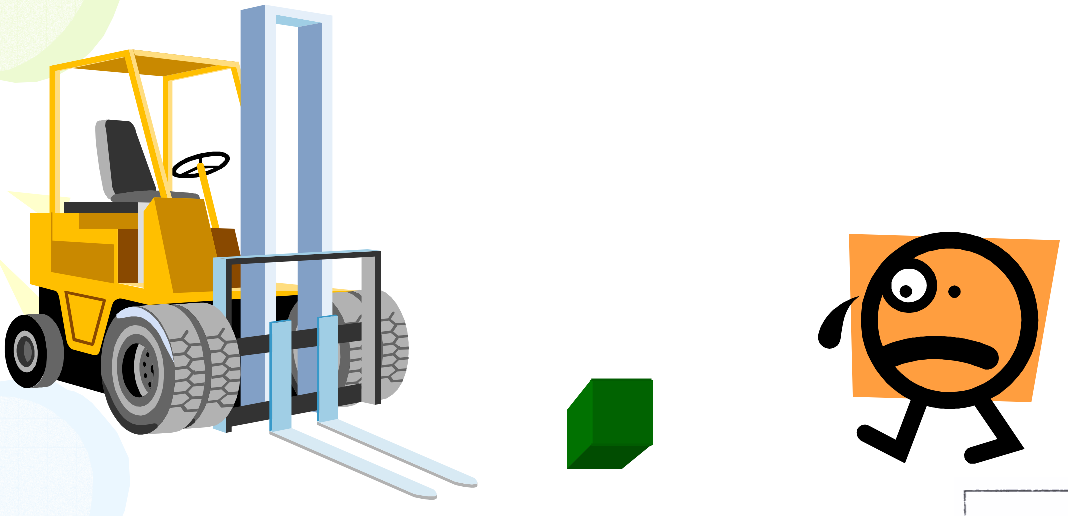
The higher the temperature of the thermal energy, the higher its quality.

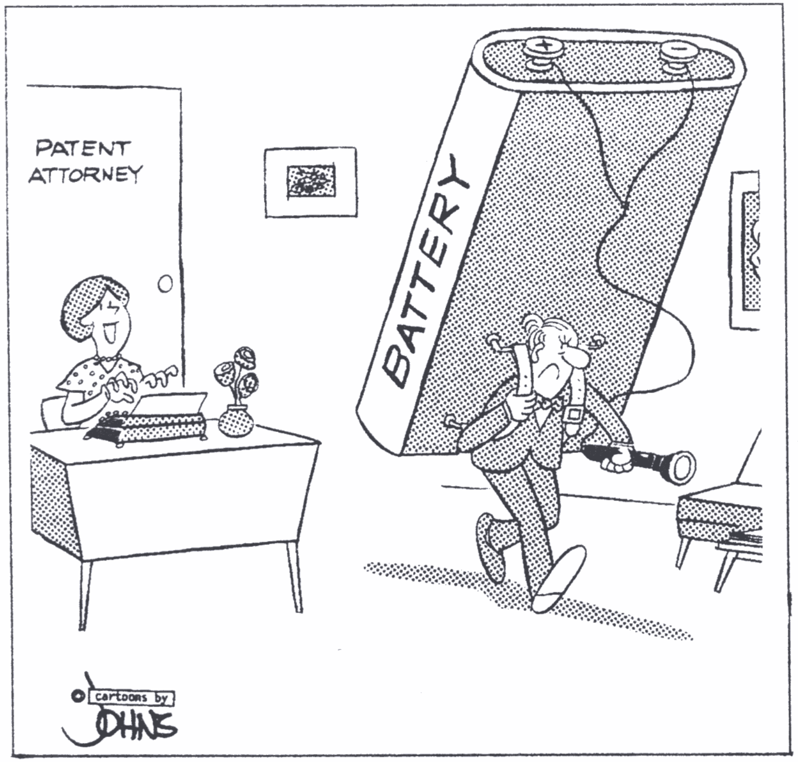
(Cengel and Boles, 2006).

The fact: High-quality (or high-temperature) energy sources, e.g. fossil fuels, are used for relatively low temperature processes like water and space heating or cooling, industrial steam production, etc.

- ✓ **Exergy efficiency permits a better matching of energy sources and uses, leading to that high-quality energy should be used for performing high-quality work.**
- ✓ **The higher the temperature, the higher the quality of the energy.**

WHICH ONE TO USE?

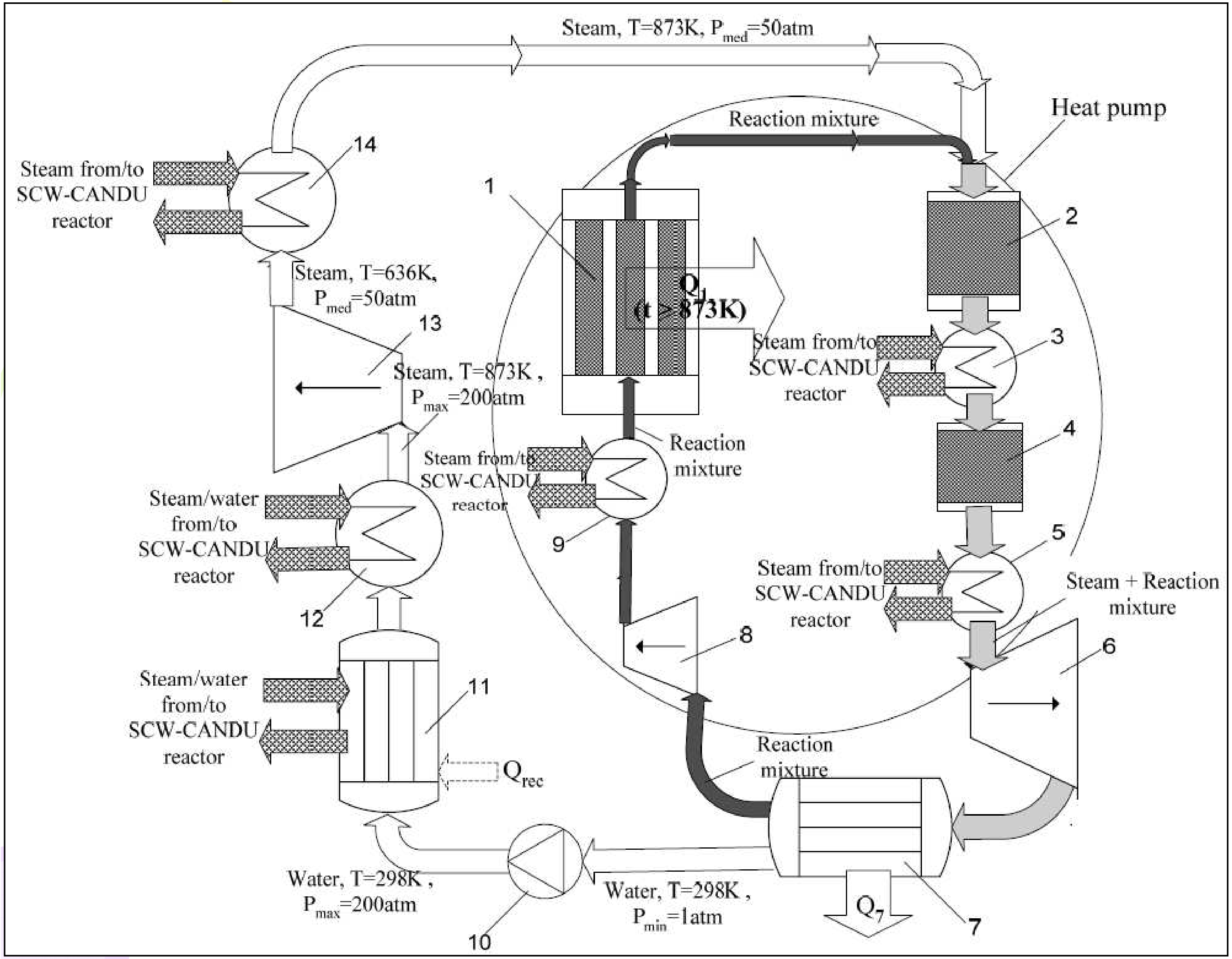




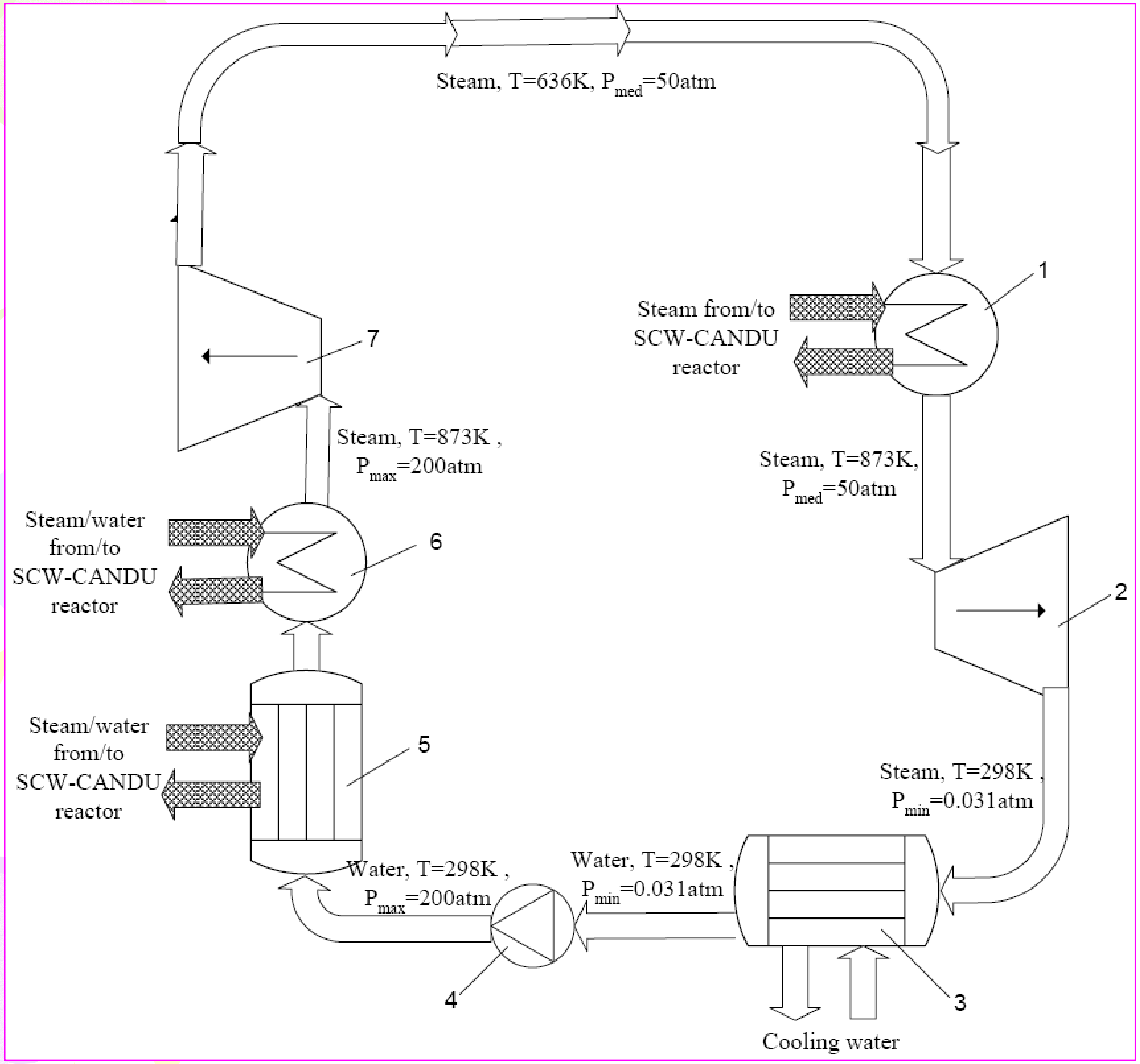
Case Study-Objectives

- To develop a new concept, using a chemical heat pump that works continuously, absorbing heat at temperatures lower than 873 K (600°C) and releasing it at higher than 873 K (600°C) for SCW-CANDU nuclear power plants.
- To employ the heat produce for use in a chemical water splitting cycle to produce hydrogen.
- To conduct a thermodynamic study to evaluate the influence of introducing the proposed heat pump on the nuclear power generation plant efficiency.

System Description



Implementation of a high-temperature heat pump into the second power generation cycle of a SCW-CANDU nuclear plant. (1: methanator; 2,4: autothermal methane converters; 3,5,9,14: reheaters; 6: low-pressure steam turbine; 7: condenser; 8: compressor; 10: pump; 11: boiler; 12: superheater; 13: high-pressure steam turbine).



Simplified schematic of the standard second power generation cycle in a SCW-CANDU nuclear plant (1: reheater; 2: low-pressure steam turbine; 3: condenser; 4: pump; 5: boiler; 6: superheater; 7: high-pressure steam turbine).

Chemical Heat Pump Concept

The operating principles of the proposed heat pump and its performance are described below. At higher temperatures, the exothermic conversion reaction of a synthesis gas (a mixture of carbon monoxide and hydrogen) to methane is carried out:

$$CO + 3H_2 \rightarrow CH_4 + H_2O + Q \qquad (1)$$

At lower temperatures, the opposite endothermic reaction for methane conversion occurs:

$$CH_4 + H_2O \rightarrow CO + 3H_2 - Q \qquad (2)$$

Reactions (1) and (2) proceeds simultaneously with the rapid water-shift reaction:

$$H_2 + CO_2 \leftrightarrow H_2O + CO \qquad (3)$$

Chemical equilibrium is shifted by changing of steam content in the reactor inputs. Reaction (1) proceeds in the methanator (device 1; Fig. 1) with a deficiency of steam and reaction (2) in the reformers (devices 2 and 4; Fig. 1) with a significant excess of steam.

ANALYSIS

→ Assumptions:

- energy losses due to mechanical friction are negligible,
- thermodynamic and chemical equilibria are achieved at the outlet of the methanator (device 1) and methane reformers (devices 2 and 4), and
- the performances of the turbines and compressors are considered ideal.

→ Property data evaluation-simplification:

- All gases except steam are modeled as ideal,
- thermodynamic data for liquid water and steam are taken from the NIST standard reference database (version 7.0),
- thermodynamic properties of others gases are taken from [11], and
- thermodynamic properties of gaseous mixtures are calculated assuming an additive input of the components.

Efficiency Investigation

Table 6 lists efficiency indicators for the compared schemes. The energy (or thermal) efficiency of the schemes are evaluated as

$$\eta_T^{(i)} = \frac{W_i}{Q_{nuc}^{(i)}} \tag{4}$$

where index i takes on a value of 1 or 2 for the schemes in Figs. 1 and 2, respectively, W_i is the work produced, and $Q_{nuc}^{(i)}$ is the heat released by the SCW-CANDU nuclear reactor and consumed by the second cycle of the overall power generation plant. Values for W and Q_{nuc} are given in Tables 2 and 3. Here, Q_{nuc} is equal to the sum of the consumed heats (taken with opposite signs) in the schemes. Taking into account that nuclear heat consumption Q_{nuc} in the scheme with a heat pump can be reduced by Q_{rec} (Table 6, column 3), its thermal efficiency can be written as follows:

$$\mathrm{\eta}_{\mathrm{T}}^{(1)} = \frac{\mathrm{W}_1}{\mathrm{Q}_{\mathrm{nuc}}^{(1)} - \mathrm{Q}_{\mathrm{rec}}} \tag{5}$$

where the indexes refer to scheme 1. The thermal efficiencies for schemes 1 and 2 are found to be 0.48 and 0.37, respectively. These data favor the standard scheme (scheme 2).

Exergy Content of Hydrogen and Efficiency

$$Ex_{H_2} = \eta_e W + Q_1 (T \geq 873K) \tag{6}$$

where Ex_{H_2} is the exergy of hydrogen; η_e is the low-temperature electrolysis efficiency; W is electrical work, and Q_1 is an external heat supply at a temperature higher than or equal to 600°C. Then the efficiency for nuclear heat utilization for hydrogen production is expressible as follows:

$$\frac{Ex_{H_2}}{Q_{nuc}} = \eta_e \left(\frac{W + Q_1/\eta_e}{Q_{nuc}} \right) = \eta_e \eta_T^{H_2} \tag{7}$$

$$\eta_T^{H_2} = \frac{W + Q_1/\eta_e}{Q_{nuc}} \tag{8}$$

Cogeneration Option

The maximum degree of such cogeneration N is estimated as follows:

$$n \leq N = \frac{Q_7 - Q_{rec}}{Q_{rec}} \tag{9}$$

where Q_7 is the heat released in the condenser of the scheme with a heat pump and Q_{rec} is the heat which could be utilized for heating a certain amount of water (20 mol in our case) in a boiler. The value $n = 0$ means no cogeneration occurs, $n = 1$ means that 20 mol of water in the standard nuclear power generation cycle are heated by the heat from the condenser of the cycle with a heat pump, and $n = N$ means that N*20 moles of water are heated in this way. Increasing values of n increases the relationship between the power capacities of the two schemes. The formulas for η_T and $\eta_T^{H_2}$ for a combined system reflect this dependence as follows:

$$\eta_T = \frac{nW_2 + W_1}{n(Q_{nuc}^{(2)} - Q_{rec}) + (Q_{nuc}^{(1)} - Q_{rec})} \tag{10}$$

$$\eta_T^{H_2} = \frac{nW_2 + W_1 + Q_1/\eta_e}{n(Q_{nuc}^{(2)} - Q_{rec}) + (Q_{nuc}^{(1)} - Q_{rec})} \tag{11}$$

where the indexes refer to scheme 1 or 2.

Table 1. Parameters for the two nuclear power plant cycles.

Power generation cycle	P_{max} **atm**	T_{max} **K**	T_1^{out} **K**	P_{med} **atm**	P_{min} **atm**	T_{min} **K**
Nuclear power generation cycle with a heat pump (Fig. 1)	200	873	873	50	1	298
Standard nuclear power generation scheme (Fig. 2)	200	873	n/a	50	0.03	298

Table 2. Work and heat flows and energy balance for the nuclear power generation cycle with a high-temperature heat pump (Fig. 1).*

	Device				
Energy	**6**	**8**	**10**	**13**	**Total**
Mechanical work, kJ (generated (+), consumed (-))	437.5	-58.6	-7.1	156.2	528.0

	Device								
	1	3	5	7	9	11,12	14	Mix**	Total
Heat, kJ (released (+), consumed (-))	94.2	-69.5	-26.0	918.2	-12.6	-1228.9	-203.07	-0.4	-528.0

* Data are given per 20 moles of water circulated in the system.

** Due to a steam enthalpy drop when decreasing its partial pressure as it is mixed with the reaction mixture, a negligible amount of heat is required to maintain a constant temperature at the inlet of methane converter 2.

Table 3. Energy balance of the standard nuclear power generation cycle (Fig. 2).*

	Device			
Energy	**2**	**4**	**7**	**Total**
Mechanical work, kJ (generated (+), consumed (-))	543.7	-7.3	156.3	692.6
	Device			
	1	3	5,6	Total
Heat, kJ (released (+), consumed (-))	-203	739.6	-1229.2	-692.6

* Data are given per 20 moles of water circulated in the system.

Table 4. Composition of the gaseous flows circulated in the high-temperature heat pump.

Devices	**Flow**	**Composition**				
		CH_4	**H_2O**	**H_2**	**CO**	**CO_2**
1	Input	0.39	0.11	2.43	0.02	0.59
	Output	0.89	1.10	0.44	0.01	0.10
2	Input	0.89	21.10	0.44	0.01	0.10
	Output	0.52	20.36	1.91	0.01	0.47
4	Input	0.52	20.36	1.91	0.01	0.47
	Output	0.39	20.10	2.43	0.02	0.59
7	Input	0.39	20.10	2.43	0.02	0.59
	Output	0.39	0.11	2.43	0.02	0.59

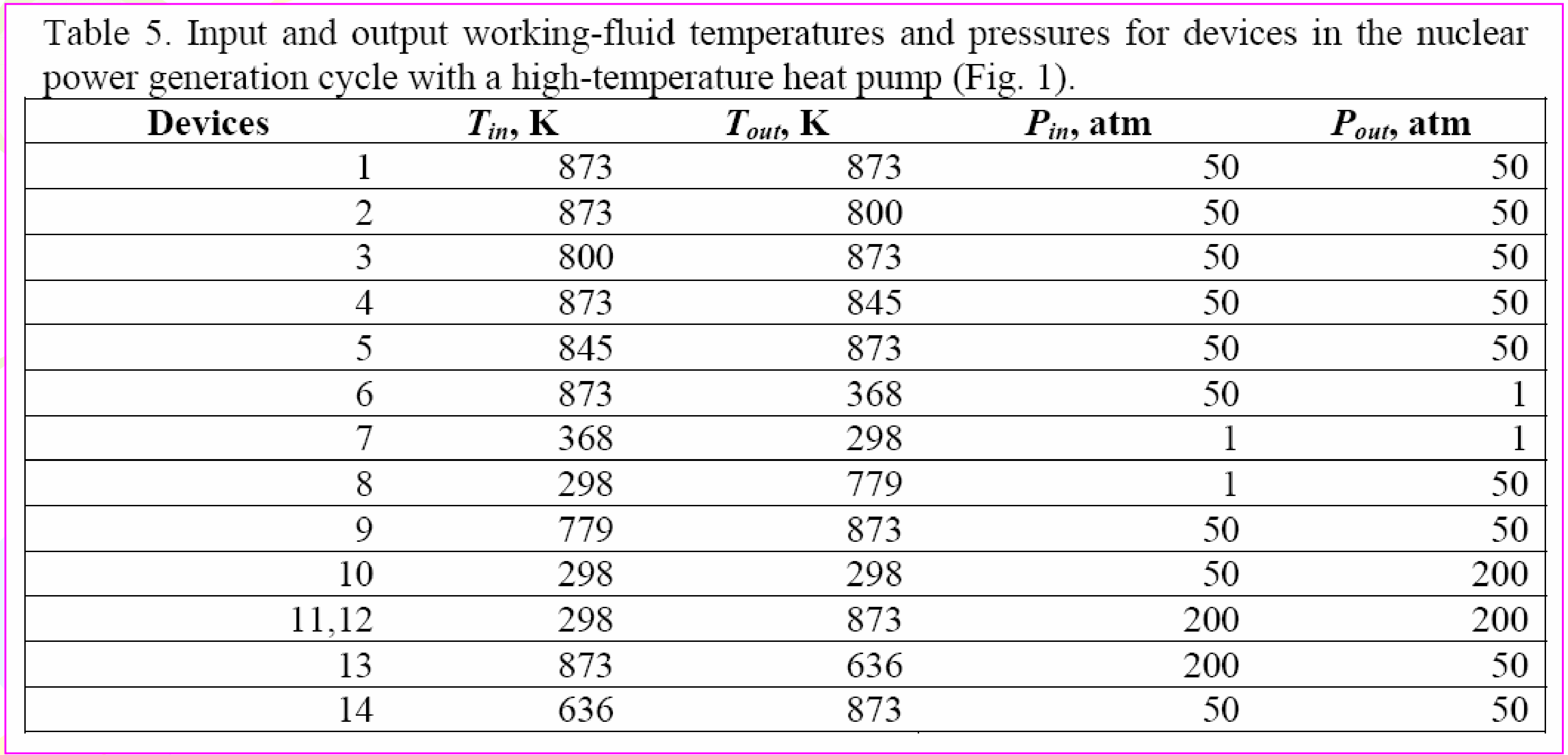


Table 5. Input and output working-fluid temperatures and pressures for devices in the nuclear power generation cycle with a high-temperature heat pump (Fig. 1).

Devices	**T_{in}, K**	**T_{out}, K**	**P_{in}, atm**	**P_{out}, atm**
1	873	873	50	50
2	873	800	50	50
3	800	873	50	50
4	873	845	50	50
5	845	873	50	50
6	873	368	50	1
7	368	298	1	1
8	298	779	1	50
9	779	873	50	50
10	298	298	50	200
11,12	298	873	200	200
13	873	636	200	50
14	636	873	50	50

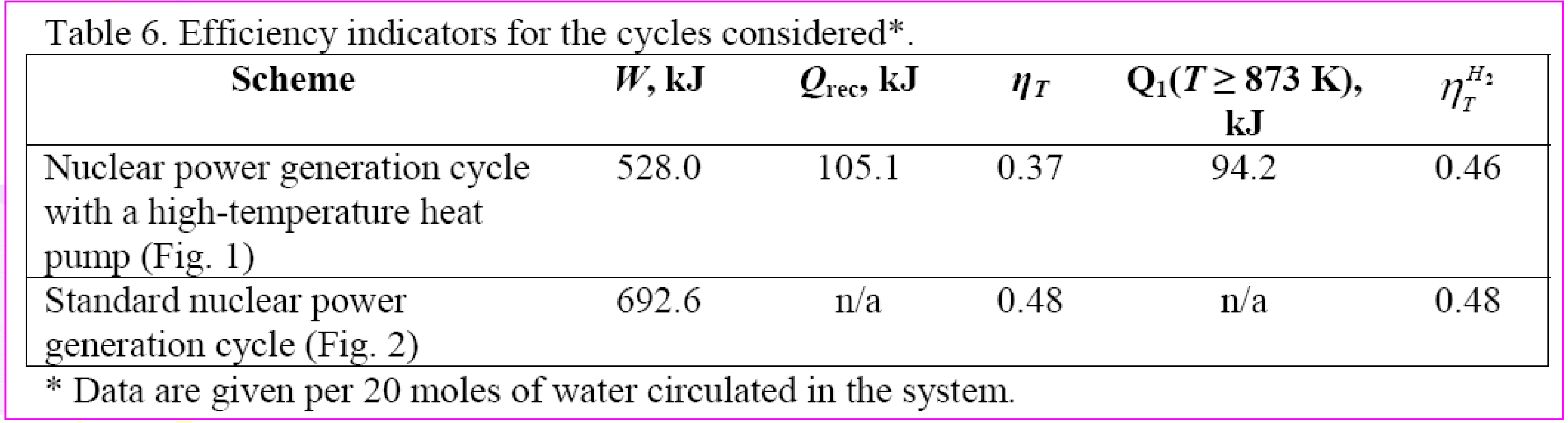
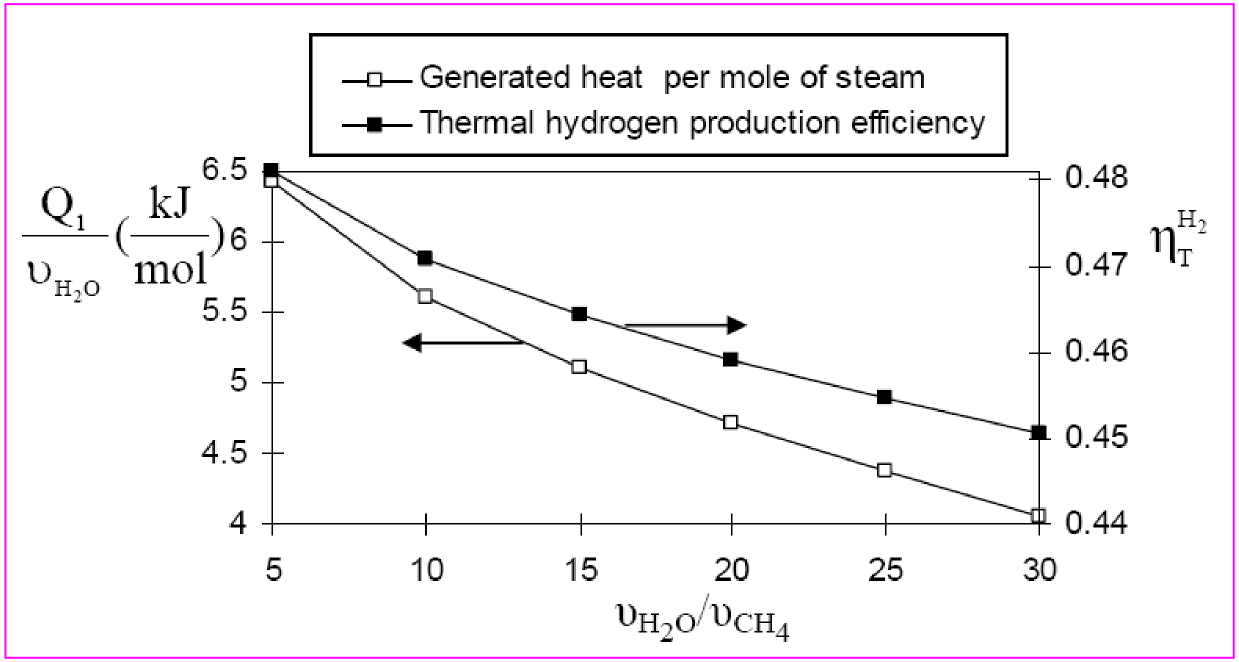


Table 6. Efficiency indicators for the cycles considered*.

Scheme	**W, kJ**	**Q_{rec}, kJ**	**η_T**	**$Q_1(T \geq 873$ K), kJ**	**$\eta_T^{H_2}$**
Nuclear power generation cycle with a high-temperature heat pump (Fig. 1)	528.0	105.1	0.37	94.2	0.46
Standard nuclear power generation cycle (Fig. 2)	692.6	n/a	0.48	n/a	0.48

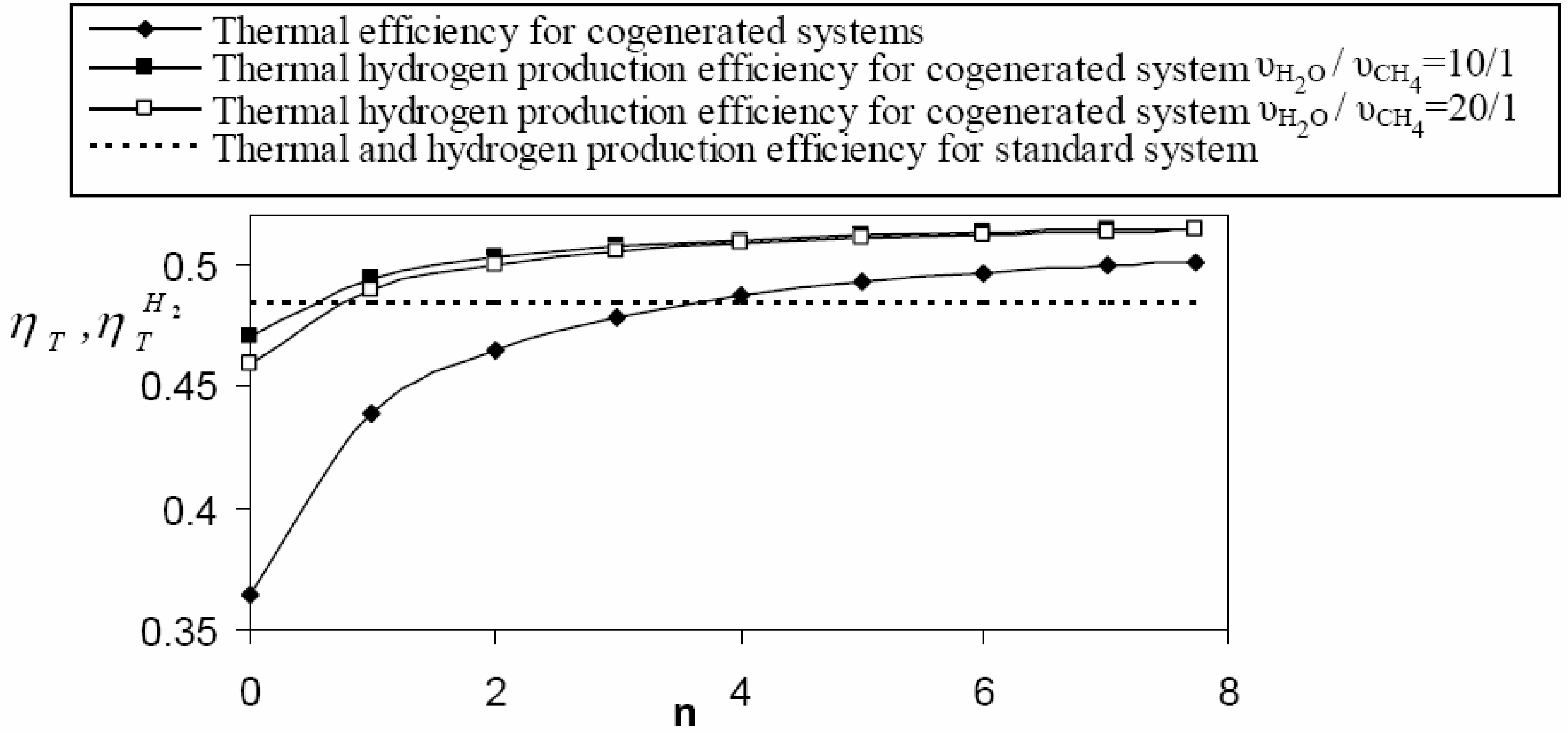
* Data are given per 20 moles of water circulated in the system.

Results



Variation of the specific heat (per mol of steam) generated in the heat pump $\frac{Q_1}{\upsilon_{H_2O}}$ and hydrogen production efficiency $\eta_T^{H_2}$

with the steam-methane ratio $\upsilon_{H2O}/\upsilon_{CH4}$ in the chemical heat pump section.



Variation of thermal and hydrogen production efficiencies η_T and $\eta_T^{H_2}$ with cogeneration degree *n*.

CONCLUSIONS

- Hydrogen economy is crucial for the future's energy picture.
- Nuclear energy should be part of a healthy energy diet.
- An advanced design of a new combined nuclear power generation plant with a chemical heat pump is proposed.
- The heat pump employs a catalytic methane conversion reaction where the reaction mixture of methane, steam, hydrogen, carbon monoxide and carbon dioxide is the working medium.
- This heat pump is implemented in the second power generation cycle of a SCW-CANDU nuclear plant.
- Further use of exergy analysis to this scheme is the subject of ongoing research.

Questions
&
Comments?